



On an additional promoting role of hydrogen in the H₂-assisted C₃H₆-SCR of NO_x on Ag/Al₂O₃: A lowering of the temperature of formation–decomposition of the organo-NO_x intermediates?

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ABSTRACT

The addition of minute amounts of H₂ to the selective catalytic reduction of nitrogen oxides (NO_x) by hydrocarbons (HC-SCR) has been shown to promote the reduction of NO_x at remarkably lower reaction temperatures on Ag/Al₂O₃ catalysts. Despite extensive investigations, the origin of this remarkable hydrogen effect is still being debated in the literature. To provide further insights into this, the desorption–reactivity of nitrates preadsorbed on a Ag (1.6 wt%)/Al₂O₃ catalyst is reported for the first time under desorbing feeds of increasing complexity. The results of these transient experiments together with those of steady-state experiments under selected gas compositions confirm some of the numerous roles of H₂ suggested previously such as being responsible for (i) changes in the distribution of Ag species, (ii) promoted HC activation and (iii) lower nitrates coverage because of their lower stability in the presence of H₂. In particular, it was found that nitrates decompose at temperatures as low as 120 °C in the presence of H₂ in the desorbing feed, instead of around 300 °C in the absence of H₂. The transient experiments in which the reactivity of the nitrates was studied under desorbing feeds containing propene (C₃H₆) as a reductant, allowed for the monitoring of the formation–decomposition of organo-NO_x species (R-NO_x). From these experiments, it can therefore be identified that another potential role of H₂ is to promote the formation–decomposition-reaction of organo-NO_x species at lower temperatures coinciding with the temperature of the onset of detection of N₂ under both transient and steady-state conditions, in line with the “chemical effect” of H₂ suggested earlier.

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1. Introduction

Public health and natural environmental concerns, partly due to the emissions of automotive exhausts and their associated pollutants such as hydrocarbons (HC), carbon oxides (CO and CO₂), nitrogen oxides (NO_x: NO and NO₂) and particulate matter (PM), have driven ever more stringent vehicle emission standards in Europe and in the USA [1,2]. These regulations require improvements of current after-treatment catalytic technologies. In particular, the removal of NO_x at lower temperatures has become extremely challenging for lean-burn and diesel powered vehicles [2], which typically operate in a large excess of oxygen. Although the ammonia selective catalytic reduction of NO_x (SCR)

and lean-NO_x trap (LNT) after-treatment catalytic technologies have been selected to meet the vehicle emission standards [2], the development of catalytic materials for direct NO_x reduction with hydrocarbons, usually referred to as Hydrocarbon Selective Catalytic Reduction (HC-SCR), would also be of interest if their performances could be improved to meet emission regulations [3].

Studying silver-alumina catalysts with various hydrocarbons in the presence of water, Miyadera was first to bring to the attention of the community that these catalysts may be promising candidates in the HC-SCR reaction [4]. These catalysts, however, suffer from insufficient performance at temperatures lower than 350 °C [4–12], which has clearly prevented their practical development to date. The Ag/Al₂O₃ system is nevertheless still the subject of in-depth investigations [3,13] as the fundamental understanding of the HC-SCR reaction at a molecular level could provide the key to designing improved Ag/Al₂O₃ catalysts. Improvement of the HC-SCR activity of the Ag/Al₂O₃ catalysts has been shown to depend strongly on (i) the Ag loading and in particular the Ag surface density of the catalysts [14], (ii) the nature of the reducing hydrocarbon,

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with oxygenated and higher hydrocarbons providing better HC-SCR performances at lower temperatures [4,5,7,9,15,16], and (iii) the preparation method, as it was reported recently that Ag/Al₂O₃ catalysts could also be prepared by ball milling [3,17–19]. The changes induced in the surface properties of the Al₂O₃ support by ball milling [3] were found to be beneficial for low-temperature C₈H₁₈-SCR in the presence of water [3,17]. The most spectacular low-temperature promoting effect on the HC-SCR reaction lies undoubtedly in the addition of a limited quantity of H₂, generally below 1%, to the reacting feeds, as was originally discovered by Satokawa et al. for light hydrocarbons [20,21]. The so-called “hydrogen effect” has been confirmed later for C₃H₈-SCR [22–24] and for HC-SCR using higher hydrocarbons [3,13,25–29]. Recently, the lowest NO_x reduction temperature in the H₂-assisted C₈H₁₈-SCR was claimed for a Ag/Al₂O₃ catalyst prepared by ball milling [3].

The origin of the hydrogen effect on the HC-SCR reaction has been intensively debated in the literature and attributed mainly to (i) changes in the distribution of the Ag species [13,22,24,29], (ii) the promotion of hydrocarbon activation to surface oxygenated compounds [13,23,24,27], (iii) the formation of reactive oxygen species such as peroxides [13,24,30], (iv) changes in the surface concentration of NO_x ad-species [13,22,23,31,32], and/or (v) the modification of chemical reactions [5,25,26]. Among NO_x ad-species, nitrates have been claimed to be reactive intermediates in the H₂-assisted HC-SCR reaction [13,23,24], although this could not be confirmed by STOS-SSITKA (Short Time On Stream-Steady State Isotopic Kinetic Analysis) in H₂-C₈H₁₈-SCR [33]. In addition, it was suggested that the formation of organo-nitrogen species (organo-NO_x), resulting from the interaction of NO_x and activated hydrocarbon ad-species, was the rate determining step of the HC-SCR [7] and H₂-HC-SCR [3] reactions. We recently came to a similar conclusion in a H₂-assisted C₃H₆-SCR kinetic investigation performed on a series of Ag/Al₂O₃ samples of various Ag loadings [34]. As it was illustrated in our earlier C₃H₆- and C₁₀H₂₂-SCR studies [35,36], the temperature at which NO_x and activated HC species interact may be estimated through transient temperature-programmed experiments in which the reactivity of NO_x ad-species is studied in the presence of hydrocarbons in the desorbing feeds. Yet the use of such an experimental approach in the HC-SCR field has been the subject of only a very limited number of investigations [10,35–42].

This work aims at investigating systematically the reactivity of nitrates adsorbed on the Al₂O₃ support of a Ag/Al₂O₃ catalyst with various NO-free H₂-HC-SCR feeds of increasing complexity, which has not been performed to date. For this purpose, C₃H₆ was chosen as a model reductant, even though higher hydrocarbons are well-known to be more representative of lean-burn or diesel engine exhausts. The results obtained in a temperature transient mode are compared to those obtained at steady state to gain further insights into the role of H₂ in the C₃H₆-SCR reaction.

2. Experimental

2.1. Catalyst synthesis and characterization

The γ-Al₂O₃ support (Procatalyse, 180 m²/g) was ground and sieved, and the fraction between 0.125 and 0.200 mm was used to prepare the Ag-promoted sample. The deposition of Ag was performed by incipient wetness impregnation of the bare Al₂O₃ support (0.7 cm³/g porous volume) with an aqueous solution of AgNO₃ (Aldrich, >99%) to achieve a silver loading of 1.6 wt%, which was ascertained by inductively coupled plasma atomic emission spectroscopy (ICP-AES, CNRS, Solaize). After impregnation, the Ag-loaded sample was aged for 4 h under ambient conditions and subsequently dried at 100 °C overnight. Finally, the Ag-loaded

sample was calcined at 600 °C (3 °C/min) for 4 h in a muffle furnace. The specific surface area of the calcined sample, measured with a Belsorp Max (Bell Japan) instrument, was found to be similar to that of the Al₂O₃ support, resulting in a Ag surface density of 0.5 Ag/nm² [14,34].

2.2. Catalytic runs

The catalytic experiments were carried out in a U-type quartz reactor (12 mm i.d.) using about 0.18 g of the Ag/Al₂O₃ sample and a total flow rate of 230 mL_{NTP} min^{−1} (~85,000 h^{−1} gas hour space velocity ~78,000 mL_{NTP} g^{−1} h^{−1} space velocity). The Ag/Al₂O₃ catalyst was held on plugs of quartz wool. The temperature of the tubular furnace was set by a Eurotherm 2408 temperature controller using a K-type thermocouple. H₂ (2%/He), NO (4000 ppm/He), C₃H₆ (2000 ppm/He), O₂ (100%), and He (100%) were fed from independent cylinders (Air Liquide) without any further purification via mass flow controllers (Brooks 5850TR). For the NO_x-TPD carried out in H₂O–O₂–He, H₂O was delivered into the gas stream through a microflow liquid mass flow controller (LO1-RAD-19-0, Bronkhorst) and vaporized in a CEM (Controlled Evaporation Mixer, W-101A-911-K, Bronkhorst) chamber, whose operating temperature was set to 80 °C. The reactor outflow was analyzed using a μ-GC (Agilent Technologies, CP4900) equipped with two channels and a combination of on-line detectors. The first channel of the μ-GC equipment, a 5A molecular sieve column (80 °C, 150 kPa He, 200 ms injection time, 30 s backflush time), was used to separate H₂, N₂, O₂, and CO. The second channel, equipped with a poraplot Q column (60 °C, 150 kPa He, 200 ms injection time), was used to separate CO₂, N₂O, C₃H₆ and H₂O. The concentrations in NO and NO₂, CO₂, N₂O, and C₃H₆ were also monitored by a NO_x chemiluminescence analyzer (Thermo Environmental Instruments 42C-HT), a CO₂ infrared detector (Maihak 710), a N₂O infrared detector (Ultramat 6 IR), and a FID detector (Thermo Environmental Instruments 51C-LT), respectively.

2.2.1. C₃H₆-SCR steady-state performances

Prior to the C₃H₆-SCR experiment, the sample was calcined in situ in O₂ (20%)–He at 500 °C (3 °C/min) for 2 h with a flow rate of 100 mL_{NTP}/min. After cooling down to 150 °C under O₂–He, the sample was submitted to a C₃H₆-SCR experiment from 150 to 500 °C [14]. The sample was subsequently exposed to the H₂–C₃H₆-SCR feed at 150 °C and the performances were measured from 150 to 500 °C [34]. Typically, the composition of the SCR feed was: 0 or 0.2% H₂, 385 ppm NO, 390 ppm C₃H₆, and 8% O₂ in He. In both SCR reactions, the temperature was increased stepwise from 150 to 500 °C with 25 °C increments and left for about 1 h at each temperature step. NO_x (NO + NO₂) conversion to N₂ was calculated as follows:

$$X_{\text{NO}_x \text{ to N}_2} (\%) = (2 \times [\text{N}_2]) / ([\text{NO}_x]_{\text{inlet}}) \times 100 \quad (1)$$

where [NO_x]_{inlet} and [N₂] were the concentrations of NO_x measured at the inlet of the reactor and of N₂ measured at the outlet of the reactor, respectively. It must be noted that minute amounts of N₂O were also formed during the SCR reactions. C₃H₆ conversion was calculated on the basis of the CO_x (CO + CO₂) products formed:

$$X_{\text{C}_3\text{H}_6} (\%) = ([\text{CO}] + [\text{CO}_2]) / ([\text{C}_3\text{H}_6]_{\text{inlet}} \times 3) \times 100 \quad (2)$$

where [CO], [CO₂], and [C₃H₆]_{inlet} were the concentrations of CO and CO₂ measured at the outlet of the reactor and of C₃H₆ measured at the inlet of the reactor, respectively.

2.3. NO oxidation steady-state performances

The activity of the Ag/Al₂O₃ sample in the oxidation of NO by molecular O₂ (385 ppm NO–8% O₂–He balance), either in the

absence or presence of 0.2% H_2 in the reacting feed, was measured from 500 to 100 °C every 50 °C by dwelling for about 30 min at each temperature step.

2.4. NO_x -TPD and C_3H_6 -TPO experiments

Temperature-programmed desorptions of preadsorbed nitrates (NO_x -TPD) were performed in various gas mixtures (O_2 -He, H_2 - O_2 -He, H_2O - O_2 -He, CO_2 - O_2 -He, C_3H_6 - O_2 -He, and H_2 - C_3H_6 - O_2 -He) which contained 8% O_2 , 0.2% H_2 , 0.2% H_2O , 390 ppm C_3H_6 , and a He balance. Prior to these NO_x -TPD experiments, the Ag/Al_2O_3 catalyst surface was saturated with nitrates following the experimental procedure used to measure the NO oxidation steady-state performances in a H_2 -NO- O_2 -He reacting feed (Section 2.3). For comparison, temperature-programmed oxidations (C_3H_6 -TPO) of C_3H_6 (0 or 0.2% H_2 -390 ppm C_3H_6 -8% O_2 -He balance) were performed on $Ag/\gamma-Al_2O_3$. Prior to the C_3H_6 -TPO experiments, the sample was pretreated in situ in H_2 (0.2%)- O_2 (8%)-He (230 mL_{NTP}/min) at 500 °C (3 °C/min) for 2 h. The catalyst temperature was then decreased to 100 °C under the same feed before being flushed with O_2 (8%)-He at 100 °C for about 15 min. The reactor was then by-passed. The reacting feed was set up and flown through the nitrates-saturated or H_2 - O_2 -He pretreated sample, and the transient experiment was started. The NO_x -TPD and C_3H_6 -TPO experiments were carried out from 100 to 500 °C, at a heating rate of 3 °C/min.

3. Results

3.1. Steady-state activity

3.1.1. C_3H_6 - and H_2 - C_3H_6 -SCR performances

Fig. 1 shows the influence of the addition of 0.2% H_2 on the C_3H_6 -SCR catalytic performance of the Ag/Al_2O_3 catalyst. For temperatures lower than 450 °C, the addition of H_2 dramatically promoted the C_3H_6 -SCR reaction in agreement with our earlier study [34] and that of Zhang et al. [43], and also with the HC-SCR studies in which various hydrocarbons were used [3,13,20–29]. The NO_x and C_3H_6 conversions in C_3H_6 -SCR were found to be shifted by about 150 °C to lower temperatures with the addition of 0.2% H_2 to the reacting feed. A steep increase in the conversions of NO_x and C_3H_6 was observed in H_2 - C_3H_6 -SCR from 150 to 300 °C. For temperatures higher than 300 °C, the conversion of NO_x remained essentially constant at about 60–70%, whereas that of C_3H_6 increased slowly from 80% at 300 °C to 100% at 500 °C. H_2 was gradually oxidized up to 225 °C, then more steeply, reaching complete consumption at 300 °C. Traces of N_2 were detected at temperatures as low as 150 °C in the H_2 - C_3H_6 -SCR, whereas N_2 was only detected at temperatures higher than or equal to 325 °C in the absence of H_2 in the feed (C_3H_6 -SCR). For temperatures higher than

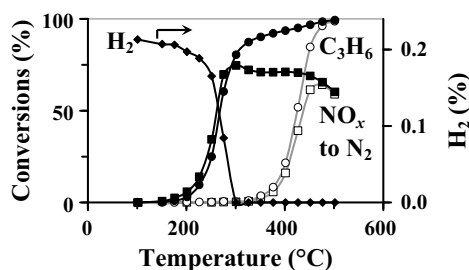


Fig. 1. Influence of the addition of 0.2% H_2 on the C_3H_6 -SCR performances. Conversions of NO_x to N_2 in C_3H_6 -SCR (□) and H_2 - C_3H_6 -SCR (●), and conversions of C_3H_6 to CO_x in C_3H_6 -SCR (○) and H_2 - C_3H_6 -SCR (●) on about 0.18 g of Ag/Al_2O_3 . Feed compositions: 0 or 0.2% H_2 , 385 ppm NO, 390 ppm C_3H_6 , 8% O_2 and He balance with a 230 mL_{NTP}/min flow rate. The concentration of H_2 in the course of the H_2 - C_3H_6 -SCR reaction is also shown (◆).

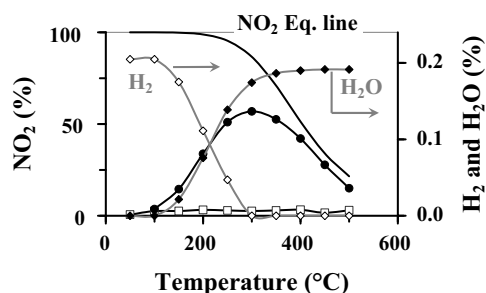


Fig. 2. NO oxidation to NO_2 in the absence (□) and in the presence (●) of H_2 on about 0.18 g of Ag/Al_2O_3 . The conversion of NO to NO_2 at equilibrium (—) and the concentrations of H_2 (◇) and H_2O (◆) are also shown. Feed compositions: 0 or 0.2% H_2 , 385 ppm NO, 8% O_2 and He balance with a 230 mL_{NTP}/min flow rate.

425 °C, the conversions of NO_x and C_3H_6 were found to be similar in both the presence and absence of H_2 .

3.1.2. NO oxidation

Under the present experimental conditions, H_2 was oxidized to H_2O at temperatures higher than 100 °C (Fig. 2). As was reported

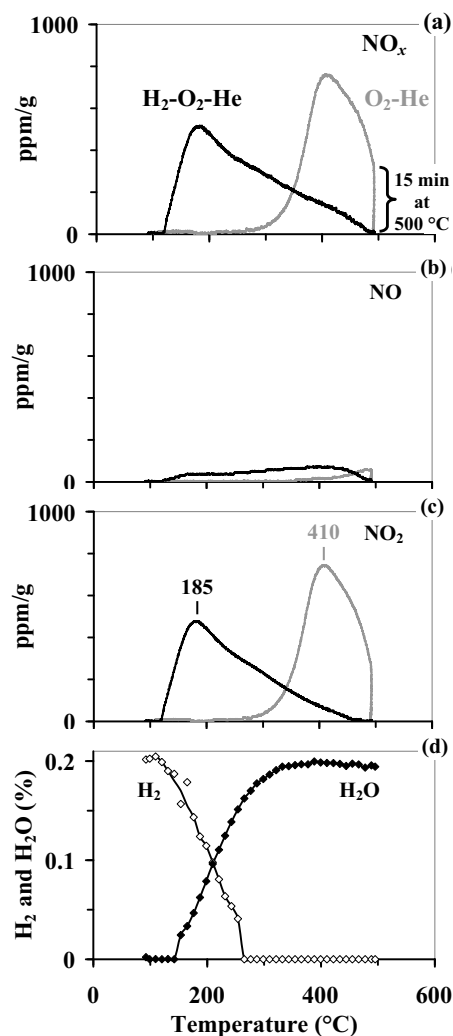


Fig. 3. Influence of the addition of 0.2% H_2 on the (a) NO_x , (b) NO and (c) NO_2 desorption profiles obtained with a rate of 3 °C/min on about 0.18 g of Ag/Al_2O_3 contacted previously with H_2 -NO- O_2 -He (0.2%-385 ppm-8%-balance) from 500 to 100 °C for 30 min every 50 °C. Feed compositions: 0 or 0.2% H_2 , 8% O_2 and He balance with a 230 mL_{NTP}/min flow rate. The concentrations of H_2 (◇) and H_2O (◆) are also shown in the course of the NO_x -TPD in H_2 - O_2 -He (d).

Table 1

Amounts of NO_x (NO + NO₂) released, N₂O and N₂ formed, and H₂ and C₃H₆ light-off temperatures (T_{LO}: defined as the temperature of 50% conversion of the reactant considered) obtained in the NO_x-TPD experiments (3 °C/min) performed under various gas compositions (8% O₂, 0.2% H₂, 0.2% H₂O, 630 ppm CO₂ and/or 390 ppm C₃H₆ in He) on about 0.18 g of Ag/Al₂O₃ contacted with NO–O₂–H₂–He (385 ppm–8%–0.2%–balance) from 500 to 100 °C for 30 min every 50 °C. 230 mL_{NTP}/min flow rate. For comparison, the light-off temperatures of H₂ and C₃H₆ obtained in the steady-state oxidation of NO (H₂–NO–O₂–He), the C₃H₆–TPO experiments and the steady-state SCR reactions are also listed in the second part of the table.

	Gas compositions	Amounts of N _i O _y species (μmol/g)					T _{LO} (°C)	
		NO	NO ₂	NO _x	N ₂ O	N ₂	H ₂	C ₃ H ₆
NO _x -TPDs	O ₂ -He	18.6	301.5	320.1	0	0	–	–
	H ₂ -O ₂ -He	59.6	259.7	319.3	0	0	210	–
	O ₂ -He + H ₂ -O ₂ -He ^a	61.7	258.3	320.1	0	0	205	–
	H ₂ O-O ₂ -He	12.1	290.0	302.1	0	0	–	–
	CO ₂ -O ₂ -He	18.6	299.6	318.2	0	0	–	–
	C ₃ H ₆ -O ₂ -He	28.7	213.4	242.1	1.8	38.0	–	–
	C ₃ H ₆ -H ₂ -O ₂ -He	13.7	127.6	141.3	8.2	79.9	260	–
	H ₂ -NO-O ₂ -He	–	–	–	–	–	210	–
	C ₃ H ₆ -O ₂ -He-TPO	–	–	–	–	–	–	470
	C ₃ H ₆ -H ₂ -O ₂ -He-TPO	–	–	–	–	–	245	420
	NO-C ₃ H ₆ -O ₂ -He-SCR	–	–	–	–	–	–	425
	NO-H ₂ -C ₃ H ₆ -O ₂ -He-SCR	–	–	–	–	–	270	270

^a The Ag/Al₂O₃ sample was first heated up to 190 °C under O₂–He before being submitted to H₂–O₂–He from 190 to 500 °C (3 °C/min). For more details the reader should refer to the caption of Fig. 4.

earlier [13,25], the addition of H₂ to a NO–O₂–He feed led to a drastic increase in the NO oxidation performance of the Ag/Al₂O₃ catalyst from 150 to 500 °C (Fig. 2), as NO was poorly oxidized in the absence of H₂ over the same temperature range (Fig. 2). The formation of NO₂ increased from 150 to 300 °C and then decreased at higher temperatures, approaching the thermodynamics predicted by the 2NO + O₂ = 2NO₂ equilibrium. The formation of NO₂ was thus found to be optimum at the temperature at which H₂ was fully oxidized, i.e. 300 °C (Fig. 2). In agreement with earlier studies [22,27,32], neither N₂ nor N₂O was formed in the course of the NO oxidation reaction performed in the presence of H₂, indicating that the role of H₂ is not to reduce NO_x on Ag/Al₂O₃ and that the reason for its promoting effect on the HC-SCR reaction must be found elsewhere.

3.2. Temperature-programmed experiments

3.2.1. NO_x-TPD

The conditions used in the present study to saturate the Al₂O₃ surface of the Ag/Al₂O₃ sample by ad-NO_x species differed substantially from those reported in our earlier works [14,34–36,38–40,44–46]. In these previous works, the samples were exposed to a NO_x–O₂–He feed at RT, whereas in the present

work the initial state of the catalyst was obtained after performing a NO oxidation reaction in a H₂–NO–O₂–He feed, for which it was shown that NO₂ was produced in significant quantities (Section 3.1.2, Fig. 2). As a NO₂–He mixture was not available, such a procedure was used to saturate the Al₂O₃ surface with nitrates, which have been suggested to be reaction intermediates in the H₂-assisted HC-SCR reactions [13,23,24].

3.2.1.1. NO_x-TPD in O₂–He. The NO_x-TPD profiles obtained in O₂–He on the Ag/Al₂O₃ sample submitted previously to a NO oxidation reaction are shown in Fig. 3a–c (gray traces). The release of the NO_x ad-species started at about 280 °C and reached a maximum at 410 °C (Fig. 3a). The NO_x-TPD profiles shown in Fig. 3 also indicate that NO_x were mainly released as NO₂ (94%, Table 1). The fact that NO_x were mainly released as NO₂ and at high temperatures is coherent with the decomposition of surface nitrates chemisorbed on Al₂O₃ [37,41,47–49]. It can also be observed in Fig. 3a–c that a temperature of about 500 °C was not high enough to allow for the complete release of NO_x from the sample. An additional period of 15 min was needed at about 500 °C to fully decompose the most strongly bound nitrates and this peculiarity accounts for the steep decreases in NO and NO₂ concentrations seen in Fig. 3b and c at about 500 °C.

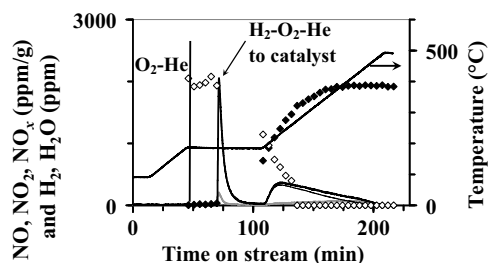


Fig. 4. NO_x -TPD profiles (NO_x : —, NO_2 : — and NO : —) obtained at 190 °C and from 190 to 500 °C on about 0.18 g of $\text{Ag}/\text{Al}_2\text{O}_3$ contacted previously with H_2 - NO - O_2 -He (0.2%–385 ppm–8%–balance) from 500 to 100 °C for 30 min every 50 °C followed by an increase in the catalyst temperature from 90 to 190 °C under O_2 -He (8%–balance). At 190 °C, the reactor was by-passed and the feed composition changed to H_2 - O_2 -He (0.2%–8%–balance). At about 70 min, the H_2 - O_2 -He mix was introduced onto the catalyst. After 40 additional minutes under the H_2 - O_2 -He mix (time on stream ~110 min), the catalyst temperature was increased (3 °C/min) to 500 °C under the H_2 - O_2 -He feed. The concentrations of H_2 (◇) and H_2O (◆) in the course of the NO_x -TPD are also shown.

3.2.1.2. NO_x -TPD in H_2 - O_2 -He. Fig. 3 compares the NO_x -TPD profiles obtained in O_2 -He (gray traces) with those obtained in H_2 - O_2 -He (black traces). In agreement with a recent work of Tamm [50] in which the influence of H_2 in an O_2 -He desorbing feed was studied to provide further insights into the influence of H_2 in the NH_3 -SCR field, the presence of H_2 clearly shifted the nitrates decomposition to much lower temperatures. The nitrates decomposition was indeed found to start at 120 °C and to be at a maximum at 185 °C in the presence of H_2 , whereas their decomposition occurred from 280 to 500 °C with a maximum at 410 °C in the absence of H_2 (Fig. 3a–c). While the amount of NO_x released in the presence of H_2 was in excellent agreement with that obtained in the absence of H_2 , about 320 $\mu\text{mol NO}_x/\text{g}$ in both cases (Table 1), that of NO was about three times higher in the presence of H_2 (59.6 $\mu\text{mol NO}/\text{g}$) compared to that found in the absence of H_2 (18.6 $\mu\text{mol NO}/\text{g}$) in the desorbing feed (Table 1). The fact that the amounts of NO_x released in both feeds were similar is consistent with earlier studies in which it was concluded that H_2 did not act as a NO_x reductant in HC-SCR [22,27,32]. It can also be noted that NO was released over a much wider range of temperatures in the presence of H_2 (120–500 °C) than in the absence of H_2 in the desorbing feed (Fig. 3b). Finally, Fig. 3d shows that the H_2 oxidation profile obtained in the NO_x -TPD transient experiment in H_2 - O_2 -He agreed with that obtained in the steady-state NO oxidation reaction (Fig. 2), the H_2 light-off temperatures being 210 °C in both cases (Table 1).

In an additional experiment, after being saturated with nitrates following the above-described NO oxidation procedure, the $\text{Ag}/\text{Al}_2\text{O}_3$ sample was exposed to an O_2 -He feed from about 100 to 190 °C (3 °C/min, Fig. 4). As expected from the NO_x -TPD experiment carried out in O_2 -He (Fig. 3, gray traces), the formed nitrates were stable in this range of temperatures (90–190 °C) and remained stored on the catalyst as no NO_x signal was detected (Fig. 4). At 190 °C, the reactor was by-passed and 0.2% H_2 was added to the O_2 -He feed. Once the composition of the H_2 - O_2 -He feed remained essentially constant, this feed was flown through the sample at 190 °C and the decomposition of nitrates was observed concomitantly (Fig. 4, ~70 min on stream). After about 40 min under the H_2 - O_2 -He feed at 190 °C (Fig. 4, ~110 min on stream), the sample was heated up to 500 °C (3 °C/min) under the same feed. The amount of NO_x released in this experiment was found to be in agreement with that obtained in the NO_x -TPD in H_2 - O_2 -He (Table 1). The NO_x -TPD experiment, in which the stability of the nitrates was investigated sequentially using firstly an O_2 -He feed up to 190 °C followed by a H_2 - O_2 -He feed up to 500 °C (Fig. 4), underlines the prominent role of H_2 in helping to decompose nitrates at much

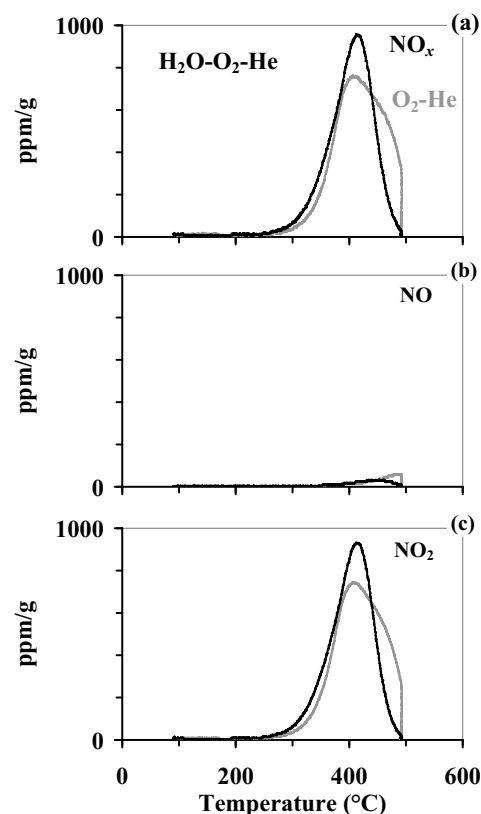


Fig. 5. Influence of the addition of 0.2% H_2O on the (a) NO_x , (b) NO and (c) NO_2 desorption profiles obtained with a rate of 3 °C/min on about 0.18 g of $\text{Ag}/\text{Al}_2\text{O}_3$ contacted previously with H_2 - NO - O_2 -He (0.2%–385 ppm–8%–balance) from 500 to 100 °C for 30 min every 50 °C. Feed compositions: 0 or 0.2% H_2O , 8% O_2 and He balance with a 230 $\text{mL}_{\text{NTP}}/\text{min}$ flow rate.

lower temperatures. Note that this effect was not observed on the Al_2O_3 support (not shown) in agreement with the earlier work of Tamm [50], which puts particular emphasis on the involvement of Ag species in this H_2 -assisted nitrates decomposition process.

3.2.1.3. NO_x -TPD in H_2O - O_2 -He. Fig. 5 shows that the NO_x -TPD profiles obtained in H_2O - O_2 -He differed only to a slight extent with those obtained in O_2 -He. The temperature at maximum NO_x desorption is indeed observed at about 410 °C in both cases. This indicates that the water formed in the course of the NO_x -TPD in H_2 - O_2 -He cannot be considered as responsible for the release of the NO_x species observed at temperatures below 300 °C in the presence of H_2 (Fig. 3, black curves). For temperatures higher than 300 °C, Fig. 5 shows that the presence of 0.2% H_2O in the desorbing feed shifted the desorption of NO_x to lower temperatures, this effect being more pronounced for the NO_x species that were released at temperatures higher than 400 °C corresponding to the decomposition of the most strongly bound nitrates. This shows that H_2O helped to partially decompose the most strongly bound nitrates. The amount of NO_x released in the NO_x -TPD in H_2O - O_2 -He was found to be close to that found in the NO_x -TPDs in O_2 -He and in H_2 - O_2 -He (Table 1).

3.2.1.4. NO_x -TPD in CO_2 - O_2 -He. The influence of CO_2 in the desorbing feed on the NO_x -TPD profiles was also investigated, as NO_x -TPD experiments were also carried out in the presence of C_3H_6 that was mainly oxidized to CO_2 under the selected experimental conditions (Sections 3.2.1.5 and 3.2.1.6). It was found that the addition of 630 ppm of CO_2 to the desorbing feed did not affect the NO_x -TPD profiles (not shown) obtained in O_2 -He (Fig. 3). Likewise,

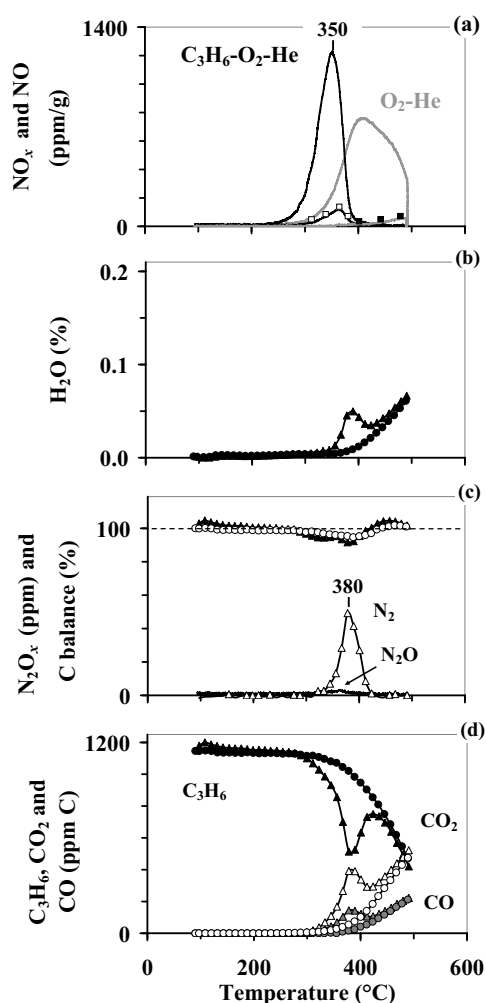


Fig. 6. Influence of the addition of 390 ppm C₃H₆ on (a) the NO_x and NO (squares) desorption profiles, (b) the H₂O traces, and (c) the carbon balances and N₂ and N₂O traces obtained with a rate of 3 °C/min on about 0.18 g of Ag/Al₂O₃ contacted previously with H₂-NO-O₂-He (0.2%–385 ppm–8%–balance) from 500 to 100 °C for 30 min every 50 °C. Feed compositions: 0 or 390 ppm C₃H₆, 8% O₂ and He balance with a 230 mL_{NTP}/min flow rate. For comparison, the traces of: H₂O (●) in (b), carbon balance (○) in (c), C₃H₆ (●), CO₂ (○) and CO (●) in (d) are also added for the C₃H₆-TPO experiment (3 °C/min) performed in C₃H₆-O₂-He (390 ppm–8%–balance) on about 0.18 g of Ag/Al₂O₃ pretreated at 500 °C for 2 h in H₂-O₂-He (0.2%–8%–balance).

the amount of NO_x released in the NO_x-TPD in CO₂-O₂-He was the same as that found in the NO_x-TPD in O₂-He (Table 1). In contrast to H₂O (Fig. 5), CO₂ therefore did not help decompose nitrates.

3.2.1.5. NO_x-TPD in C₃H₆-O₂-He. The presence of C₃H₆ in the desorbing feed had a marked influence on the NO_x-TPD profiles. Firstly, NO_x and NO releases (Fig. 6a) occurred at lower temperatures in the NO_x-TPD experiment carried out in C₃H₆-O₂-He compared to that carried out in O₂-He, the temperatures of maximum release of NO_x being 350 and 410 °C, respectively. Secondly, the NO_x desorption peak was narrower in the presence of C₃H₆ and the amount of NO_x released was lower (242.1 μmol NO_x/g, Table 1) than that released in the absence of C₃H₆ (NO_x-TPD in O₂-He, 320.1 μmol NO_x/g, Table 1). The latter observation indicates that the NO_x species were partially converted to N₂ and N₂O (Fig. 6c) in the course of the NO_x-TPD in C₃H₆-O₂-He. Table 1 shows that the NO_x species were mainly converted to N₂ (38.0 μmol N₂/g compared to 1.8 μmol N₂O/g) and that the amount of N species (NO + NO₂ + 2N₂O + 2N₂) released in the NO_x-TPD in C₃H₆-O₂-He (321.7 μmol N/g, Table 1) was similar to the amount of NO_x released in the NO_x-TPD in O₂-He

(320.1 μmol N/g, Table 1). N₂ started to be produced at 320 °C in the NO_x-TPD in C₃H₆-O₂-He (Fig. 6c), in agreement with the temperature of the onset of detection of N₂ in the steady-state C₃H₆-SCR (Fig. 1), and peaked at 380 °C. Excess consumption of C₃H₆ (Fig. 6d), and excess productions of H₂O (Fig. 6b) and CO_x (Fig. 6d) were observed in the NO_x-TPD in C₃H₆-O₂-He compared with the C₃H₆-TPO experiment (Fig. 6d) for which C₃H₆ oxidation was studied in the absence of preadsorbed nitrates. Moreover, the carbon balance in the NO_x-TPD in C₃H₆-O₂-He experiment (Fig. 6c) was found to be slightly more deficient than that found in C₃H₆-TPO (Fig. 6c) from 290 to 400 °C, thus indicating some additional HC storage on the catalyst in the presence of preadsorbed nitrates. These observations indicate that C₃H₆ and/or its derivatives such as partially oxidized species interacted with the preadsorbed nitrates at temperatures as low as 250 °C (Fig. 6a, black curve) with the resulting formation of organo-NO_x species. This explanation is consistent with the earlier work of Yu et al. [41] in which these authors concluded that organo-NO_x species were formed at temperatures as low as 233 °C with the interaction of NO_x and C₃H₆ on a Ag (5 wt%)/Al₂O₃ catalyst. For temperatures between 250 °C and 320 °C, the latter temperature corresponding to the temperature of the onset of detection of N₂ (Fig. 6c), the formed organo-NO_x species decomposed mainly to NO₂ and traces of NO (Fig. 6a).

3.2.1.6. NO_x-TPD in C₃H₆-H₂-O₂-He. Fig. 7 compares the profiles observed in the NO_x-TPD in C₃H₆-H₂-O₂-He to those observed in the NO_x-TPD in H₂-O₂-He (Section 3.2.1.2) and in the C₃H₆-H₂-O₂-TPO experiments. It can be seen that the addition of C₃H₆ to the desorbing feed in the NO_x-TPD performed in the presence of H₂ did not shift the NO_x desorption profile to lower temperatures (Fig. 7a), as was observed in the absence of H₂ (Fig. 6a). The NO_x-TPD profiles were indeed found to be similar up to about 160 °C in both the presence and absence of C₃H₆ (Fig. 7a). At higher temperatures, however, the amount of NO_x released in the NO_x-TPD in C₃H₆-H₂-O₂-He (141.3 μmol NO_x/g, Table 1) was found to be much lower than that found in the NO_x-TPD in H₂-O₂-He (319.3 μmol NO_x/g, Table 1). This is attributed to the reduction of NO_x to N₂ and N₂O in the presence of C₃H₆ in the desorbing feed (Fig. 7c and Table 1). It is also of interest to note that the temperature at which N₂ started to be detected in the NO_x-TPD in C₃H₆-H₂-O₂-He (~150 °C, Fig. 7c) closely matches that at which N₂ was detected in the H₂-C₃H₆-SCR reaction (Fig. 1). Regarding H₂ oxidation, Table 1 shows that the light-off temperature of H₂ was about 210 °C in the NO_x-TPDs in H₂-O₂-He and in NO oxidation in H₂-NO-O₂-He, whereas the presence of C₃H₆ in the feed in the C₃H₆-H₂-O₂-TPO experiment delayed the light-off temperature of H₂ to 245 °C (Fig. 7c and Table 1). This suggests that C₃H₆ competes for the sites responsible for H₂ oxidation. As was also observed in the absence of H₂ in the desorbing feed (Fig. 6c and d), the maximum in the consumption of C₃H₆ and in the productions of CO_x (Fig. 7d) was observed concomitantly with the maximum production of N₂ at 260 °C (Fig. 7c) in the NO_x-TPD in C₃H₆-H₂-O₂-He. The C₃H₆ light-off temperature was found to decrease to a significant extent in the presence of H₂ both in the TPO and the SCR experiments (Table 1). Finally, regarding the C balance, it was found that the presence of H₂ favored the storage of hydrocarbons at temperatures lower than 250 °C (Fig. 7c) compared to the experiments performed in the absence of H₂ (Fig. 6c). Hydrocarbon storage was also found to be more pronounced in the NO_x-TPD in C₃H₆-H₂-O₂-He than in the C₃H₆-H₂-TPO for temperatures lower than 240 °C (Fig. 7c). Between 250 and 280 °C, the C balance became positive in the NO_x-TPD in C₃H₆-H₂-O₂-He, which was not observed in the C₃H₆-H₂-TPO, and this temperature domain coincided with that for which maximum production of N₂ was observed (Fig. 7c).

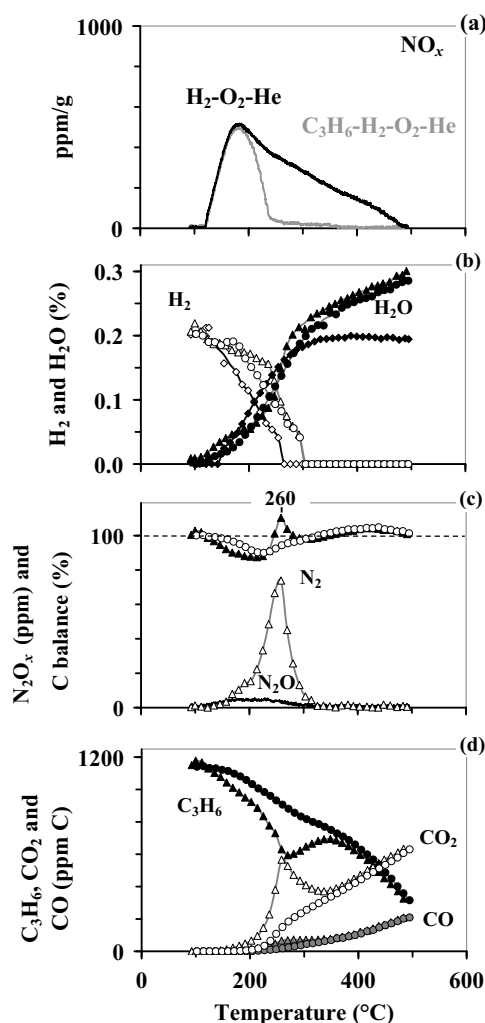


Fig. 7. Influence of the addition of 390 ppm C₃H₆ on (a) the NO_x desorption profile, (b) the H₂ (Δ) and H₂O (▲) traces, and (c) the carbon balance (▲) and N₂ (Δ) and N₂O (—) traces obtained with a rate of 3 °C/min on about 0.18 g of Ag/Al₂O₃ contacted previously with H₂-NO-O₂-He (0.2%–385 ppm–8%–balance) from 500 to 100 °C for 30 min every 50 °C. Feed compositions: 0 or 390 ppm C₃H₆, 0.2% H₂, 8% O₂ and He balance with a 230 mL_{NTP}/min flow rate. For comparison, the traces of (i) H₂ (—○—) and H₂O (—●—) in (b), carbon balance (○) in (c), C₃H₆ (●), CO₂ (○) and CO (●) in (d) are also added for the C₃H₆-TPO experiment (3 °C/min) performed in C₃H₆-H₂-O₂-He (390 ppm–0.2%–8%–balance) on about 0.18 g of Ag/Al₂O₃ pre-treated at 500 °C for 2 h in H₂-O₂-He (0.2%–8%–balance) and (ii) H₂ (—◇—) and H₂O (—◆—) in the NO_x-TPD in H₂-O₂-He (0.2%–8%–balance) extracted from Fig. 3d.

4. Discussion

In agreement with earlier studies in the field of HC-SCR with various hydrocarbons [3,5,13,21–23,25–29,32,34,43], the reduction of NO_x by C₃H₆ in an excess of O₂ was found to be drastically promoted by the addition of 0.2% H₂ to the reacting feed (Fig. 1). The much higher NO oxidation performance of the Ag/Al₂O₃ catalyst in the presence of H₂ (Fig. 2) provides an indirect indication of the occurrence of changes in the distribution of the different types of Ag species in the catalyst. It is indeed generally acknowledged that oxidation reactions, such as NO oxidation, occur preferentially on Ag metal clusters, whereas the reduction of NO_x to N₂ occurs on oxidized Ag species [12,51]. Such changes in the distribution of the Ag species in Ag/Al₂O₃ catalysts have been reported in many different HC-SCR studies [12,13,24,26,27,29,32]. Yet the fact that these changes only account for the promoting effect of H₂ in the HC-SCR reactions is still being debated [13,26,27,32]. The production of NO₂ over these reduced Ag clusters has been ruled out as the origin of

the promoting effect of H₂, as it has been shown that the H₂-HC-SCR performance of Ag/Al₂O₃ catalysts was lower when NO₂ was fed as a reactant instead of NO [13,22].

Another interesting influence of H₂ in the desorbing feed concerns the stability of the preadsorbed nitrates. Fig. 3 clearly shows that the preadsorbed nitrates are released at much lower temperatures in the presence of H₂ on the Ag/Al₂O₃ sample. This result is consistent with those reported recently by Tamm [50]. In the present work, it was possible to define precisely the temperature at which the adsorbed nitrates started to be released in the presence of H₂ (120 °C, Fig. 3). According to the NO_x-TPD experiment in which the stability of the preadsorbed nitrates was studied in the presence of H₂O (Fig. 5), the much lower stability of the preadsorbed nitrates in the presence of H₂ (Fig. 3) cannot be attributed to the production of H₂O via H₂ oxidation in the NO_x-TPD in H₂-O₂-He. It is also of importance to note that H₂ did not affect the stability of the preadsorbed nitrates on the bare Al₂O₃ support (results not shown), as was also reported by Tamm [50]. The lower stability of the nitrates formed on Ag/Al₂O₃ is thus dependent on the concomitant presence of H₂ and Ag, and can be attributed to a redox process (2NO₃[−] + H₂ = 2NO₂ + 2OH[−]) involving Ag species. This lower stability was also illustrated in the NO_x-TPD experiment in which the temperature of the Ag/Al₂O₃ sample was raised up to 190 °C under an O₂-He feed before H₂ introduction (Fig. 4). As expected from the results of Fig. 3, no NO_x was released in the absence of H₂ up to 190 °C and the adsorbed nitrates were stable under this particular atmosphere (Fig. 3). As soon as H₂ was introduced at 190 °C, however, part of the nitrates was rapidly decomposed (Fig. 4). Such a fast transient reactivity of nitrates is consistent with the results reported by Tamm [50] using a cycling methodology at 250 °C. These experiments (Figs. 3 and 4) clearly indicate that the nitrates stability strongly decreased in the presence of H₂. Such a conclusion is consistent with the FTIR study of Kannisto et al. [31] which showed an increase in the intensity of the absorption bands attributed to surface nitrites and nitrates upon the removal of H₂ from the NO_x feeds at 350 °C on Ag/Al₂O₃. From the present study and that of Tamm [50] however, it cannot be formally concluded whether this particular phenomenon results (i) from the migration of the nitrates adsorbed on Al₂O₃ toward the Ag species and their reduction by the H species (Fig. 8, pathway a) or (ii) from the reduction of the nitrates located on Al₂O₃ from the migration of the H species located on the Ag species (Fig. 8, pathway b). The scheme reported in Fig. 8 is also consistent with one of the potential roles of H₂ reported in earlier literature, which has been proposed to result in a lower coverage of the catalyst surface by the nitrates [5,9,12,23,25,28].

The steady-state HC-SCR, the C₃H₆-TPO and the NO_x-TPD experiments performed in the present work (Figs. 1, 6 and 7), also confirmed the promoting effect of H₂ on HC activation in agreement with earlier works [13,23–25,27,28,43]. The C₃H₆ light-off temperature was indeed found to decrease to a significant extent with the addition of H₂ in the C₃H₆-TPO experiments (from 470 to 420 °C, Table 1) and the steady-state HC-SCR (from 425 to 270 °C, Table 1). Moreover, it was found that HC storage occurred at much lower temperatures in the presence of H₂ in the C₃H₆-TPO experiment (Fig. 7c, carbon balance in the 150–300 °C range) than in the absence of H₂ (Fig. 6c, carbon balance in the 300–425 °C range). Former FTIR studies also concluded that the storage of HC, in the presence of H₂, as partially oxidized species (C_xH_yO_z) such as acetates and enolic species was enhanced [9,12,13,43]. In the experiment in which the Ag/Al₂O₃ sample was saturated with nitrates and their desorption-reaction was studied in the presence of both H₂ and C₃H₆ in the desorbing feed (NO_x-TPD in H₂-C₃H₆-O₂-He, Fig. 7), it was found that the presence of preadsorbed nitrates enhanced HC storage at lower temperatures compared to the C₃H₆-H₂-TPO (Fig. 7c, carbon balances in the 120–250 °C range). This indicates

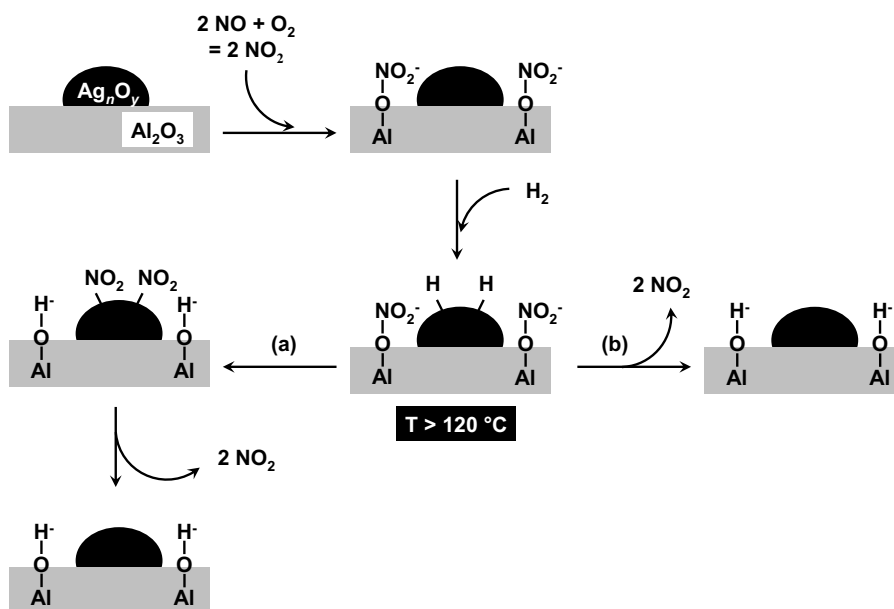


Fig. 8. Schematic representation of the H_2 -assisted decomposition of nitrates of $\text{Ag}/\text{Al}_2\text{O}_3$. Ag_xO_y represents Ag species of undefined composition.

that C_3H_6 not only was activated as $\text{C}_x\text{H}_y\text{O}_z$ species but also reacted with the stored nitrates to form organo- NO_x (R-NO_x) species at temperatures as low as 120°C . Such R-NO_x species were found to decompose at temperatures higher than 250°C in the absence of H_2 in the desorbing feed (NO_x -TPD in C_3H_6 - O_2 -He, Fig. 6) and to be responsible for the observed release of NO_2 at temperatures lower than those found in the NO_x -TPD in O_2 -He (Fig. 6a). In the presence of H_2 in the desorbing feed, N_2 was formed at temperatures as low as 150°C (Fig. 7a), in good agreement with the onset of detection of N_2 in the steady-state H_2 - C_3H_6 -SCR experiment (Fig. 1). This indicates that the further transformation of the R-NO_x species eventually leads to the formation of N_2 under these conditions. The optimum conditions of the decomposition-reaction of the R-NO_x species were found to occur at a temperature of 260°C , the temperature at which N_2 production (Fig. 7c) peaked and an excess carbon balance (Fig. 7c) was observed in the NO_x -TPD experiment in H_2 - C_3H_6 - O_2 -He. It is remarkable that this temperature matches rather well with that at which maximum production of N_2 (275°C) was observed in the steady-state H_2 - C_3H_6 -SCR experiment (Fig. 1). It can therefore be identified from the present study that another potential role of H_2 is to promote the formation-decomposition-reaction of organo- NO_x species at lower temperatures, as this step has been suggested to be rate determining in the HC-SCR process [7,34]. This potential role of H_2 would be perfectly in line with the “chemical effect” of H_2 suggested originally by Burch and co-workers [3,5,25,26].

5. Conclusion

The desorption-reactivity of nitrates preadsorbed on a Ag (1.6 wt%)/ Al_2O_3 catalyst is reported for the first time under desorbing feeds of increasing complexity. The results of these transient experiments together with those of steady-state experiments under selected gas compositions confirm some of the numerous roles of H_2 suggested previously such as (i) changes in the distribution of the Ag species, (ii) promoted HC activation and (iii) lower nitrate coverage because of their lower stability in the presence of H_2 . In particular, it was found that nitrates decompose at temperatures as low as 120°C in the presence of H_2 in the desorbing feed, instead of around 300°C in the absence of H_2 . The transient experiments in which the reactivity of the nitrates was studied

under desorbing feeds containing propene (C_3H_6) as a reductant, allowed for the monitoring of the formation-decomposition of organo- NO_x species (R-NO_x). From these experiments, it can therefore be identified that another potential role of H_2 is to promote the formation-decomposition-reaction of organo- NO_x species at lower temperatures coinciding with the temperature of the onset of detection of N_2 under both transient and steady-state conditions, in line with the “chemical effect” of H_2 suggested earlier [3,5,25,26].

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